

An Evaluation Of Methods For Passivating Silicon Integrated Circuits

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Providing adequate protective films for silicon integrated circuits is becoming increasingly important. The glass used to insulate or "passivate" these devices contributes greatly to their reliable performance. A number of contaminants and environmental stresses can easily convert the commonly used n-type surface of semiconductor devices to p-type, leading to a degradation of transistor characteristics. One well known form of degradation occurs when sodium ions (salts) are accidentally introduced into the thin silicon dioxide surface of transistors and then are diffused into close proximity with the silicon surface (figure 1). This may take place under the influence of the electrical field and be aided by relatively high temperatures and humidity. To guard against such failures, it has become an almost universal practice to deposit comparatively thick (1.5-micron or greater) layers of glass or other inorganic materials over the silicon structure.

Additional reasons for depositing reliable inorganic insulators have come into prominence recently. For semiconductors such as germanium and gallium arsenide, thermally grown oxides do not provide an adequate insula-

tion or diffusion barrier. Other means must be found to provide a suitable dielectric film.¹ Such films provide mechanical protection against accidental abrasion that can occur during lead bonding and encapsulation.² They also may be used as capacitors, either as separate elements of the integrated circuit structure or, in some instances, as integral parts of MOS (metal-oxide-silicon) transistors.³ As integrated circuits become more complex, there is an increasing need for additional insulating layers on the surface (figure 2) to isolate lines of conductors which "cross over" on the way to output terminals.

Criteria for Selection

Several desirable qualities can be specified as criteria for film selection:

- Adhesion
- Stability and lack of grain structure
- Freedom from cracks, pinholes, etc.
- Low ion mobility
- High electrical resistivity
- High dielectric constant (when appropriate)
- Etching convenience

The need for adhesion is obvious and obtainable in most instances if adequate predeposition cleaning steps are followed. Difficulties here occur mostly with films that are highly stressed, due either to intrinsic stresses or to a mismatch in thermal expansion coefficients.

Stability and lack of grain structure is a more subtle criterion that is frequently overlooked when lists of suitable materials are compiled. As a rule, any recrystallization or devitrification of a thin film will leave grain boundaries or voids which form easy routes of access to the surface to be protected. This is sufficient reason in many instances to reject standard crystalline ceramics (alumina, for example) as prospective materials.

Cracking is generally a manifestation of structural instability or high internal stresses. Tensile stresses are most deadly, since they cause cracks or voids when relieved. This seems to occur when thick layers of silicon nitride Si_3N_4 undergo densification when prepared, for example, by pyrolytic decomposition.⁴ On the other hand, silicon dioxide, with its very low coefficient of thermal expansion, is regularly used with comparatively high

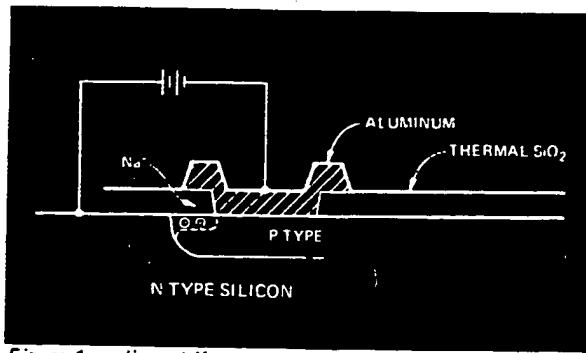


Figure 1, sodium drift near a silicon p-n junction.

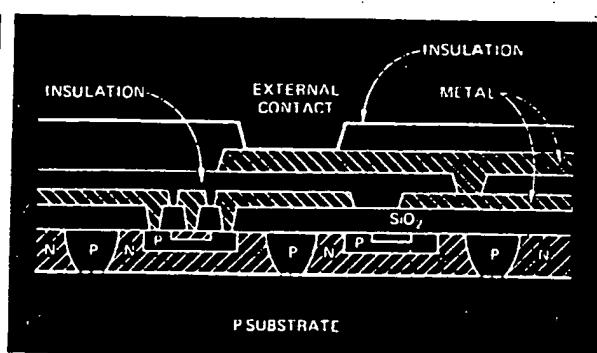


Figure 2, multiple layers of metallization and insulation.

expansion materials such as silicon and aluminum in situations where, because of high temperature processing, extremely high compressive stresses occur.

Materials with low ion mobility can prevent sodium contamination. Low ion mobility is also useful for any diffusion-masking material. The diffusing ions cannot penetrate the masking material to any great extent during the time-temperature cycle when "dopant" is being diffused into the semiconductor surface.

The requirement for high electrical resistivity is not stringent. A value of 10^{12} ohm-cm will suffice for most applications.

Ordinarily, a high dielectric constant is a disadvantage, because it increases spurious capacitance linkages in devices. However, in MOSFET devices and MOS integrated circuits, a high dielectric constant for the gate insulation offers an advantage in device performance. This has suggested the use of Si_3N_4 and Al_2O_3 , either alone or in composites, rather than SiO_2 .

Another criterion frequently overlooked in choices of insulators is the need for a convenient process of etching or otherwise forming patterns or openings in the thin layers. The most widely practiced method is to form a photoresist mask over the surface and then to etch holes down to the contacts to be exposed. The ease of this procedure with SiO_2 or related glasses, using HF solutions and the same photoresists employed in forming the diffusion masks, has made these materials favorites for use as passivation or

insulation layers. However, the reactivity of the dielectric must naturally be considered in the light of other etchants used during fabrication. Since aluminum, for example, is generally etched into conductor patterns as part of the fabrication of integrated circuits, the etch rate of any suitable protective insulator in aluminum etchant must be small.

Suitable Materials

Largely because of their stability and lack of grain structure, amorphous inorganic insulating materials have been used most frequently for passivation. SiO_2 , SiO_2 -based glasses, Al_2O_3 , and Si_3N_4 are the favorites in this category. Pertinent properties of these materials are summarized in table 1.

Silicon dioxide films have been used extensively for years as a part of silicon transistor technology. Thermally grown layers are generated to serve as diffusion masks. The final grown layer is usually left to provide insulation between the silicon surface and the evaporated conductor stripes which serve as interconnections. More recently, SiO_2 film deposited at low temperatures has been considered both as a protective layer and as an insulation between multilayer conductor patterns.

SiO_2 -based glasses have, from time to time, been used for integrated circuits, generally because of a need to improve some characteristic of pure SiO_2 . Mixed phosphorous oxide-silicon dioxide glasses, for example, are

known to block alkali ions better than pure SiO_2 .⁶ Also, various constituents have been added to lower the working temperature of SiO_2 . One way to provide a coating of SiO_2 glass is to apply a fine powder of frit to the surface and then apply heat until the powder reflows into a continuous layer.¹ However, only multicomponent, lower melting point glasses can be used with this technique, since the wafers cannot be heated to a temperature above 577°C (the aluminum-silicon eutectic temperature) without risk of a damaging reaction between the aluminum conductor and the diffused silicon surface.

Multi-component glasses have been considered as a means of providing a closer match in thermal expansion coefficient to that of silicon, aluminum, and other metals. The expansion coefficient of pure SiO_2 is about $5 \times 10^{-7}/^\circ\text{C}$; silicon, $30 \times 10^{-7}/^\circ\text{C}$; and aluminum, $125 \times 10^{-7}/^\circ\text{C}$. Available glasses can usually be found with expansion coefficients throughout the range from $5 \times 10^{-7}/^\circ\text{C}$ to approximately $100 \times 10^{-7}/^\circ\text{C}$.⁶ An obvious difficulty in using multicomponent glass is the need to control stoichiometry during the deposition process. It also sometimes is difficult to obtain commercial glasses free from alkali impurities.⁷ Finally, the glass chosen must be chemically durable with respect to the etchants and environments to which it is exposed.

There has been considerable interest in dielectric materials other than SiO_2 and various silicate glasses. Most attention has been devoted to two materials, silicon nitride and aluminum oxide. The latter has attracted interest because of its relatively high dielectric constant (typically 7.7 to 8.5 in thin film form) which offers a performance advantage when used as the gate insulation in MOS devices. Surprisingly, films of Al_2O_3 deposited at low temperatures by sputtering or reactive evaporation are amorphous and easily etchable in HF solutions.⁷ Unfortunately, any heat treatment of these films at temperatures over about 400 - 500°C results in recrystallization and at the same time renders the films unetchable by normal chemical techniques.⁸ It is necessary to resort to sputter etching or other novel techniques to a
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TABLE 1 - CHARACTERISTICS OF DIELECTRIC MATERIALS FOR THIN FILM APPLICATIONS

Material	Remarks
SiO_2	Relatively high alkali mobility. High thermal expansion mismatch. Etching convenience.
SiO_2 -based glasses	Process limitations in maintaining stoichiometry and stability. Purity limitations. Less chemical durability.
Al_2O_3	Recrystallization with high temperature processing. Novel etching techniques. Lower ion mobility Higher dielectric constant.
Si_3N_4	Novel etching techniques. Lowest ion mobility. High internal stresses (sometimes).

an techniques to open patterns in these films. Silicon nitride has many of the same advantages and disadvantages as aluminum oxide. It is known to be superior to SiO_2 and is probably superior to Al_2O_3 as a diffusion mask⁹ and as a barrier to alkali ion drift. However, silicon nitride is chemically etchable only in hot H_3PO_4 (180°C), which means a considerably more complex SiO_2 masking and etching operation is required as part of the procedure for making patterns.¹⁰ Silicon nitride has also sometimes exhibited tendencies to crack as a result of non-uniform internal stresses when deposited, for example, by chemical vapor deposition.⁴

Deposition Processes

There are several methods for depositing thin films: evaporation, chemical vapor deposition, sedimentation/glass "firing," and RF sputtering. To be useful for passivation, a method should meet the following criteria:

1. Deposition at moderate temperatures; for silicon devices, there is always an upper limit imposed by the alloying of metal contacts, diffusion, etc.
2. Deposition at rates in the area of hundreds of angstroms per minute to avoid prohibitively long runs.
3. Practicality in the sense of compatibility with inexpensive large-scale production.

In the past, thermal evaporation was the preferred process for depositing dielectric films. Compounds such as SiO_2 , MgF_2 , etc., have a vapor pressure high enough to allow conventional evaporation sources to be used. The disadvantages of these materials (non-reproducibility, stress, cracking, sensitivity to

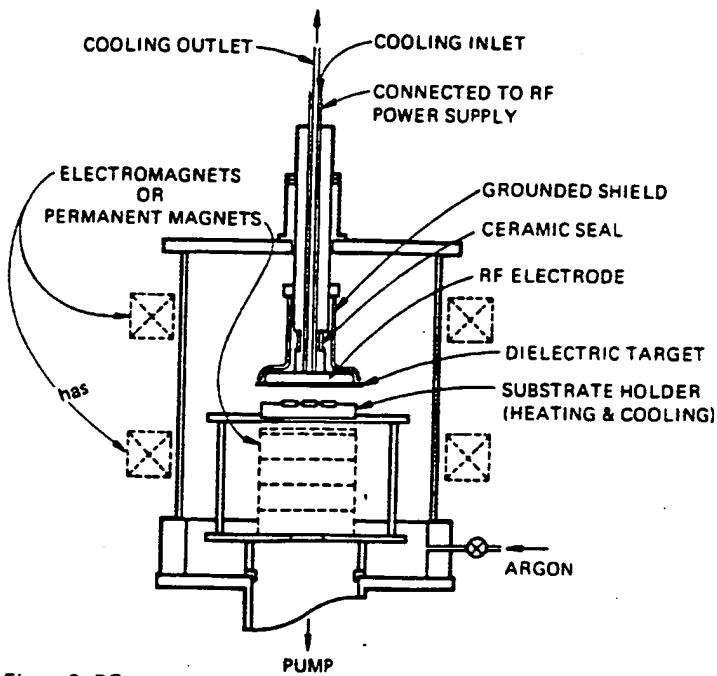


Figure 3, RF-sputtering system.

TABLE 3 – TRANSISTOR RELIABILITY WITH SPUTTERED SiO_2 FILMS COMPARED WITH A BOROSILICATE GLASS

Film	Hours on Test	Sample Size	Type of Test	Incidence of Failures
				Reverse Forward
SiO_2 hot	1000	76	150°C back bias	0 0
		76	T & H back bias	2 0
SiO_2 cold	1000	72	150°C back bias	0 0
		72	T & H back bias	0 0
Sedimented borosilicate glass	1000	116	150°C back bias	6 1
		116	T & H back bias	0 0

atmospheric exposure) have increased recent interest in glassy materials which cannot be readily evaporated. SiO_2 , for example, cannot be easily evaporated because it fractionates ($2\text{SiO}_2 \rightarrow 2\text{SiO} + \text{O}_2$) and has a low vapor pressure in the temperature range of conventional sources. Materials such as SiO_2 can be made in thin film form by techniques such as vapor deposition, firing of a glass frit, and RF sputtering.

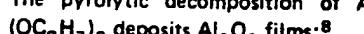
Vapor deposition has come to be widely used for depositing SiO_2 , Si_3N_4 , Al_2O_3 , and other more exotic dielectric materials. Recent developments have emphasized the need for reduced depositon temperatures. One method of reducing temperature is to supply energy in the form of a glow discharge. This permits a lowering of the surface temperature from 1000°C

to 300°C for silicon nitride.¹¹

Silicon dioxide has been vapor deposited by the pyrolytic decomposition of tetra-ethoxy silane and other alkoxysilanes:¹

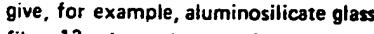


The pyrolytic decomposition of $\text{Al}(\text{OC}_3\text{H}_7)_3$ deposits Al_2O_3 films:⁸



Mixed-phase glassy films can be deposited by incorporating more than one volatile compound into the reactor to give, for example, aluminosilicate glass films.¹²

Amorphous silicon nitride films can be made by the pyrolytic reaction of silane and ammonia which is carried out in a hydrogen atmosphere:¹³



The application of a fired glass frit is a relatively inexpensive and easy tech-

TABLE 2 – DEPOSITION RATES BY RF SPUTTERING
(5" DIA DISK, 0.8 KILOWATTS INPUT)

Material	Deposition Rate
SiO_2	1200A/min
GSC-1 glass (alumino-boro-silicate)	700
Pyrex	500
191 CP glass (alumino-calcium-silicate)	400
Alumina	400
Boron nitride	300

nique to use if the temperature and compositional constraints can be tolerated. Generally, the glass is applied by centrifuging a fine suspension of particles in a mixture of ethyl acetate and isopropyl alcohol into a device wafer, and then fusing the deposited glass.¹⁴ The small particle size (about 1000Å) and the high degree of compaction obtained by centrifuging permit 1-micron films to be formed by firing for a few minutes at or somewhat below the softening point of the glass, where the viscosity is equal to $10^7.6$ poise. This allows the film to flow in a continuous layer under the influence of surface tension and form a pinhole-free film that offers a high degree of thickness control, typically about ± 2 percent for a 1.5-micron film.

In the past few years, RF sputtering has gained wide acceptance as a method of depositing insulators. This technique may be used with any dielectric for which a suitable electrode plate can be made. Compositional control of complex solid solutions, such as the SiO_2 -based glasses, is relatively easy to obtain. Neither the sputtering target nor the substrates to be coated need be heated to over a few degrees above ambient, and deposition rates fall well within the practical range (100-1000Å/minute) shown in table 2.15

A schematic cross-section of an RF system is shown in figure 3. Important influences on the quality of the deposits are the presence or absence of magnetic fields, the argon pressure, target-to-substrate spacing, and the electrical linkage between the substrate holder and electrical ground.¹⁶ These parameters, along with the RF input power, are known to influence the electrical potentials and ion bombardment which occur on the surface of the wafers. Of importance in a fundamentally different way is the temperature of the substrates.

Techniques for Film Testing

Several techniques have been developed to compare SiO_2 -based films deposited by various methods. Obtaining comparative data with transistors is extremely expensive, in terms of time as well as money, and its usefulness is limited. Table 3 shows a

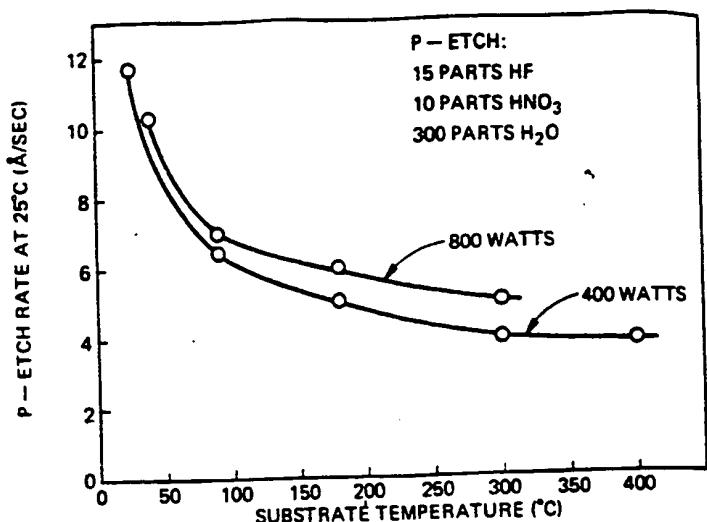


Figure 4, effect of substrate temperature on P-etch rate (magnetic field intensity at target = 100 gauss).

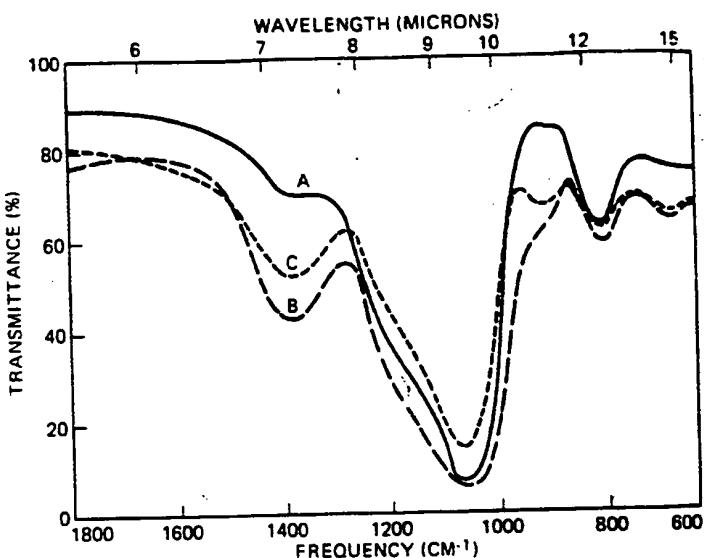


Figure 5, infrared spectra showing effects of target surface removal and run-in time on mixed-composition glass films: (A) GSC-1 film RF-sputtered from a fire-polished GSC-1 plate; (B) film sputtered from same plate after removal of the outer layer of the plate by grinding; (C) film sputtered from same plate after grinding and run-in period.

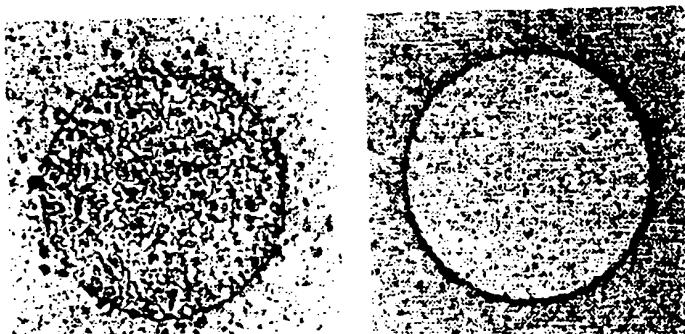


Figure 6, holes in SiO_2 films obtained by etching; their appearance is compared for materials of different quality ("bad" on left, "good" on right).

sample of data¹⁷ which illustrates the problems that arise when transistor reliability is used as a sole measure of quality.

To compare the reliability of sputtered SiO_2 (deposited both on a hot (450°C) wafer and on a cold (150°C) wafer) with the reliability of a sedimented borosilicate glass requires many transistors for adequate statistics (528 in table 3). It also requires considerable time (1000 hours \cong 6 weeks), even when accelerated aging conditions shown like those shown in table 3 are used. ("T & H" in the table means 85°C temperature and 85% relative humidity; the back bias voltages, 3 volts emitter/10 volts collector, were applied during the entire time.) Finally, the answers obtained are (1) relative to a specific device and (2) statistical in content. The data as shown in table 3, for example, can only be taken to mean that the three passivation layers are roughly equivalent in performance. The difference in the number of failures was not judged to be statistically significant by those familiar with this type of testing.

Because of the difficulties and cost of this sort of reliability testing, a number of different, simpler techniques have been used to examine and evaluate films. It should be emphasized that no single technique by itself characterizes a film sufficiently, and none is an adequate substitute for device testing.

Differences in glass composition, bond strain, and density can be determined by means of a selective etch¹⁸ called "P-etch" (a solution of 15 parts

49% hydrofluoric acid, 10 parts 70% nitric acid, and 300 parts water), which has been used effectively in evaluating silicon dioxide and various glass films. For example, a glass film of low density or a film with a high degree of bonding strain will etch relatively fast in P-etch. Table 4 shows a comparison of the P-etch rate for specimens of nominally pure SiO_2 prepared by various techniques.^{19,20} Figure 4 shows the effect of substrate temperature on the P-etch rate for RF-sputtered SiO_2 . The lower etch rate at higher temperatures is believed to correlate with a higher density and a lower bond strain at high temperatures.

The index of refraction is influenced by a film's density and composition; the greater the refractive index, the greater the film index. The refractive index is also increased either by oxygen deficiency or the presence of various contaminants in the glass. Sample data¹⁷ for RF-sputtered SiO_2 and for thermally grown SiO_2 are shown in table 5. Again, a comparison shows that the 450°C substrate film is closer to thermally grown SiO_2 than is the 100°C substrate film. The higher refractive index is believed to be due mainly to a slight oxygen deficiency.

Infrared spectroscopy is probably the simplest method for comparing films of similar composition. The presence of water, impurities, deviations from stoichiometry, and bond strain can be revealed in this way. An example¹⁷ of the use of these spectra is provided by figure 5 which shows traces for three different sputtered films of General Electric GSC-1 glass (a high melting borosilicate glass). The band at 1390 cm^{-1} is attributed to B-O stretching, and the band at 1070 cm^{-1} to Si-O stretching. Therefore, the relative intensity of these two bonds is a measure of the boron-to-silicon ratio in the films. Spectrum A of figure 5 shows an RF-sputtered film made from a GSC-1 glass plate which, in effect, had been fire polished during fabrication. Spectrum B is of a film sputtered from a target whose outer skin had been ground away. The intensity of the band at 1390 cm^{-1} indicates that the film corresponding to spectrum A is boron deficient, and so, presumably, the outer layer of the

GSC-1 target was boron deficient. It is good practice to have some "run-in" time for RF sputtering whenever a target is used for the first time, as shown by comparing spectrum B with spectrum C. The boron composition of the film with greater "run-in" time (spectrum C) is closer to that of bulk GSC-1 glass.

Another sensitive measure of SiO_2 film quality is the "PBUT" phenomenon.²¹ When holes are etched in SiO_2 films as part of the fabrication of multilayer integrated circuits, it is common practice to use an etchant of known characteristics, such as buffered HF (300 gm NH_4F , 60 cm^3 conc. HF, 450 $\text{cm}^3 \text{H}_2\text{O}$). This allows etching for a known film thickness to be terminated at just the right depth. In the course of such work it was discovered, from etch rate measurements made over larger areas, that holes often etched through much faster than expected. In addition, microscopic examinations showed that the etching had occurred very unevenly. Examples of holes etched in "normal" (right) as well as "bad" (left) SiO_2 films are shown in figure 6. To allow a more quantitative measure of this phenomenon, the following approach can be taken: If the substrate is a conductor, use the copper decoration technique to reveal pinholes in thin insulating films. In the figure 6 example, attempts were made to copper plate the insulating film. In regions where pinholes existed, the copper plated out in the form of tiny spheres.

Attempts to decorate the as-deposited films invariably revealed very few pinholes. However, if a film was repeatedly etched in buffered HF and, after each etch step, an attempt was made to decorate, it was found that the density of decorated sites increased quite suddenly from near zero to a substantial quantity. This sudden increase in decorated site density occurred between etch steps differing in thickness by only 1000 Å. The remaining thickness of glass at which this first occurs is called the Pinhole Break-Up Thickness (PBUT). A more general figure of merit for SiO_2 film quality is thus the ratio of the PBUT to the total film thickness, a quantity called the "PBUT ratio."

TABLE 4 - P-ETCH RATES FOR VARIOUS PASSIVATIONS OF SiO_2

Method	P-Etch Rate
Anodic oxidation	18-230 Å/sec
Evaporation	20-70
RF sputtering	4-12
Pyrolytic decomposition	6-20
Thermal oxidation	2

TABLE 5 - REFRACTIVE INDEX OF SiO_2 FILMS

Sample	Subst. Temp.	R.I. (5461 Å)
RF SiO_2	100°C	1.476
RF SiO_2	450°C	1.473
Thermal SiO_2	980°C	1.461 ¹⁸

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An example of the correlation of the PBUT ratio with sputtering pressure is shown in table 6. The etching uniformity (as measured by the PBUT ratio) can show a remarkable pressure dependence over the range from 5 to 20 millitorr.

X-ray fluorescence is a particularly appropriate technique when one is attempting to analyze for heavy atoms in a comparatively light atom film. For example, argon (atomic number 18) can be measured quantitatively without too much difficulty in films containing only atoms of low atomic number, such as oxygen (A.N. 8), nitrogen (7), silicon (14), and aluminum (13). Data of this sort for sputtered SiO_2 is shown in figure 7.22. This plot shows that the amount of argon incorporated in the films ranges from over 10 percent at about 0°C

substrate temperature to a very small amount at 450°C.

In table 7, several properties of SiO_2 films sputtered in three different modes are compared to thermally grown, standard SiO_2 . Comparing films B and C to thermally grown SiO_2 shows that a film containing a high concentration of argon (B) can have properties (notably the P-etch rate) closer to thermal oxide than one with

a low argon content (C). We can only conclude that the effect of argon on the properties of sputtered SiO_2 is small compared to the effect of other processes occurring during deposition, such as thermal annealing and bombardment "annealing."

In summary, the importance of diffusion masking, crossover insulation, and surface passivation of semiconductor devices has generated great interest in the comparative quality of thin film insulators. A combination of techniques can be used to evaluate a film's composition, structure, and chemical stability. No one technique in itself is sufficient, but a combination can show a great deal about pertinent characteristics of any insulator under consideration.

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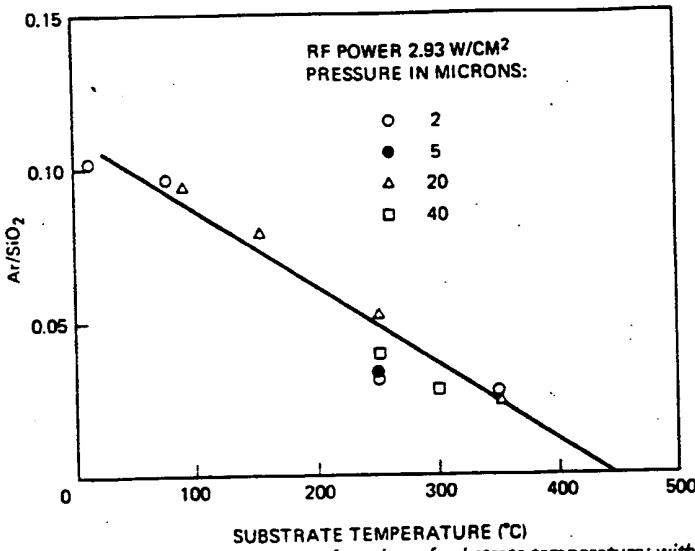


Figure 7, argon concentration as a function of substrate temperature; with magnetics, close (1.125 in.) spacing.

TABLE 7 - COMPARISON OF THERMALLY GROWN AND SPUTTERED SiO_2 FILMS

Property	Thermally Grown SiO_2 with magnets	Sputtered SiO_2		
		Film A (2.93 W-cm ⁻² rf power: 10 microns pressure: 300°C)	Film B (2.93 W-cm ⁻² rf power: 10 microns pressure: 300°C; without magnets)	Film C (2.93 W-cm ⁻² rf power: 40 microns pressure: 300°C; without magnets)
Ar/SiO ₂	-	0.03	0.009	0.001
P-etch rate, ¹⁵ °A/min	120 at 25°C	325 at 24°C	280 at 22°C	3800
Density	2.20	2.28	2.16	1.98
Refractive Index (at = 5461 Å)	1.461	1.47		1.465